PACKAGE OF COLOR PHOTOGRAPHIC FILM

FIELD OF THE INVENTION

The present invention relates to a package of color photographic film exhibiting enhanced storage stability, in which package the film is subjected to be a hermetically-sealed package inside a moisture proof envelope.

BACKGROUND OF THE INVENTION

In recent years, with the intent of saving of resources, reduction of waste materials, product weight reduction and cost reduction, simplification of packaging materials has been widely carried out. In the traditional package of color photographic film, the film is packed and purchased in a polyethylene canister. After the roll is taken for photographic processing, the container has no

further function and goes to waste. It is possible to recycle it, but it is bothersome.

A package of color photographic film which employs a moisture proof envelope, eliminating the polyethylene canister, is disclosed, for example, in Unexamined Japanese Patent Publication (hereinafter, referred to as JP-A) 2001-142177. In that invention, described are resource saving, waste reduction, reduction in weight and size of packaging materials, as well as cost reduction.

However, the package of this proposal has proven that storage stability of the color photographic film is inadequate under harsh environmental conditions. Specifically, it was found that in the package, there is a drawback of deterioration of layer adhesiveness of photographic constitution layers against extreme and repeated changes of temperature. The cause is the extreme change of temperature is directly transferred to the photographic film through the thin moisture proof envelope and a metallic film magazine, whereby the physical properties of layers are affected, due to lack of the traditional polyethylene canister.

Therefore, the problems to be solved in the present invention are to enhance environmental benefits by

simplification of the packaging materials of the color photographic film package, and further, to provide a package of color photographic film which exhibits improvement of the drawback in storage stability along with simplification of packaging materials.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a package of color photographic film which exhibits improved storage stability.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram showing an example of a package of color photographic film of the present invention.

Fig. 2 is a schematic diagram showing an example of a package of color photographic film employing a plastic canister.

DETAILED DESCRIPTION OF THE INVENTION

The foregoing object of the present invention can be accomplished by the following embodiments.

(1) A package of color photographic film comprising:

a strip of color photographic film which is wound onto a spool, and is packed in a metallic film magazine which provides light shielding, and then the packed film is hermetically sealed in a moisture proof envelope, in place of a plastic canister,

wherein a subbing layer provided between a substrate and a photographic constitution layer of the color photographic film has a dry layer thickness of 0.05 to 0.30 μm, and comprises a binder containing a gelatin as a main component.

(2) The package of color photographic film of (1) above, wherein the gelatin contained in the binder for the subbing layer has a magnesium ion content of not more than 500 ppm.

(3) The package of color photographic film of (1) or (2) above, wherein the moisture proof envelope exhibits a moisture permeability of not more than 20.0 $g/m^2 \cdot 24h$ (at 40 °C·90% RH), and an oxygen permeability of not more than 2,000 $ml/m^2 \cdot 24\ h \cdot 101kPa$.

(4) The package of color photographic film of any one of (1) - (3) above, wherein the moisture proof envelope is made of an aluminum evaporated plastic film.

(5) The package of color photographic film of any one of (1) - (4), wherein the substrate of the color photographic film is an acetyl cellulose ester substrate having an acetylation degree of 2.6 to 3.0.

(6) The package of color photographic film of any one of (1) - (5), wherein the color photographic film comprises a substrate, having thereon an anti-halation layer, light sensitive layers and non-light sensitive layers,

wherein the anti halation later is provided closest to the substrate of photographic constitution layers, and

each of the light sensitive layers of red, green and blue sensitive layers comprises at least two layers.

(7) The package of color photographic film of any one of (1) - (6), wherein the subbing layer comprises a gelatin having a magnesium ion content of 5 to 100 ppm.

(8) The package of color photographic film of any one of (1) - (7), wherein the color photographic film is hermetically sealed, and the packaged film is packed in a paper-board box.

As a result of diligent study, the inventor of the present invention discovered that the above problems were eliminated by employing a package of color photographic film, in which a strip of color photographic film was wound onto a

spool, and the wound film was packed in a metallic film magazine to provide light shielding and then the packed film was hermetically sealed in a moisture proof envelope employing no resin canister, wherein a subbing layer provided between a substrate and a photographic constitution layer of the color photographic film had a dry layer thickness of 0.05 - 0.30 μm, and comprised a binder containing gelatin as a main component. This enabled the inventor to achieve the present invention.

An example of a configuration of the package of color photographic film of the present invention is shown in Fig.1. In Fig. 1, "1" is a light-shielded, packed color photographic film, "2" is a thermoplastic resin pouch, and "3", "4" and "5" are heat-sealed portions to structure the package of color photographic film of this invention employing a thermoplastic resin film for the pouch. "6" is an opaque container. That is, the package of color photographic film of this invention comprises a package of light-shielding photographic material, in which the package is hermetically sealed using a transparent thermoplastic film, and the opaque container to pack the forgoing package. Further, the package shown in Fig. 1, in which a photographic material is hermetically sealed, is made of a sealed package employing a

sheet of thermoplastic film and heat-sealing it at three locations. In this case, since heat-sealed portion "4" is at the center of the package, this method is known as a center seal method.

Correspondingly, Fig. 2 is a schematic diagram showing an example of the package of color photographic film, employing a common plastic canister which is traditionally used in the art. The color photographic film is hermetically sealed in a plastic canister consisting of body 7 and cap 8, also made of plastic, for moisture proofing, after which the film is packed in an opaque container 6 made of paper-board. The material of the moisture proof envelope employed in this invention may be a generally used thermoplastic resin film, as long as it satisfies the requirement of exhibiting moisture permeability of 20.0 $g/m^2 \cdot 24$ h (at 40 °C·90% RH) or less, and oxygen permeability of not more than 2,000 $ml/m^2 \cdot 24$ h·101 kPa.

Specifically, preferred are a metal-laminate film, matalized film, and thermoplastic resin film having an inorganic compound deposited layer described in JP-A 6-95302. An inorganic compound deposited layer is described in Usumaku Handbook (Handbook of Thin Films), pp. 879 - 901, edited by Japan Society for the Promotion of Science; Shinku Gijutsu

Handbook (Handbook of Vacuum Technology), pp. 502 - 509, pg. 612 and 810, published by The Nikkan Kogyo Shimbun, Ltd.; Shinku Handbook, zoteiban (Handbook of Vacuum, enlarged and revised edition), pp. 132 - 134, published by Ulvac, Inc.

The thickness of the moisture proof envelope of this invention is basically 30 - 400 μm, preferably 40 - 200 μm, but more preferably 60 - 200 μm.

In this invention, a canister made of a resin employed as part of the packaging materials for color film is not used, which is primarily for enhancement of ecological consideration.

In this invention, it is possible to market the package of color photographic film in the state of: the strip of color photographic film is wound on a spool, after which the film is packed in a metallic film magazine to provide light shielding, and then the packed film is hermetically sealed in a moisture proof envelope, employing no plastic container, and further, the moisture proof envelope carries a printed commercial design. Alternatively, the color photographic film packed in the moisture proof envelope without printing of commercial design on it, can be packed in a paper-board box carrying a commercial design.

The paper-board box employed in this invention may be a box made from common paper pulp. Specifically, it is preferable to employ recycled paper pulp, because it enhances ecological concerns.

Storage stability is assured by the following embodiments, which exhibits a package of color photographic film with simplified packaging materials and enhanced ecological concerns employing the moisture proof envelope, instead of a resin canister.

The subbing layer of the photographic film of this invention is placed between a substrate and a photographic constitution layer of the color photographic film, which enhances adhesiveness of both layers.

In this invention, the dry layer thickness of the subbing layer is 0.05 - 0.30 μm, but preferably 0.07 - 0.20 μm. In cases when it is thinner than this range, adhesiveness is reduced, and when it is too thick, desired characteristics of the photographic film tend to be adversely affected.

The binder comprised mainly of gelatin of this invention means that the weight ratio to the total weight of the binder is 50% or more, but preferably 55% - 100%.

In a binder comprised mainly of gelatin, binders to be mixed with the gelatin are not specifically limited, and almost any appropriate polymer may be employed. In the present invention, cellulose ester polymer is preferred, and specifically, diacetyl cellulose is preferably mixed to effectively meet the objects of this invention. Further, to the subbing layer, mixed may be various additives, such as a surface active agent and a hardening agent.

Gelatin employed for a binder of the subbing layer of this invention preferably exhibits a magnesium ion content of at most 500 ppm.

Basically, gelatin contains various impurities derived from the raw material. Impurity ions are generally eliminated by an ion exchange treatment. However, to achieve the objects of this invention, the inventor discovered that it was important to closely control the amount of magnesium ions, but not potassium ions and sodium ions. Even when the amount of a magnesium ion is large, the objects of this invention can be achieved by controlling the amount of magnesium ions within the range of this invention.

Namely, the subbing layer of this invention is formed by employing gelatin having a magnesium ion content of no more than 500 ppm, preferably in the range of 5 - 100 ppm,

but specifically preferably 5 - 50 ppm. Further, after coating and drying of the photographic constitution layers on the subbing layer containing significantly lower amount of magnesium ions, the photographic film is preferably produced at a magnesium ion content in the gelatin binder of the subbing layer to result in no more than 500 ppm, preferably in the range of 5 -100 ppm, but specifically preferably 5 - 50 ppm.

When color photographic film is produced, a magnesium compound may be employed during a precipitation-washing processing in the preparation process of the light sensitive silver halide emulsion, which is incorporated in the photographic constitution layer. However, in the case of this invention, it is important that not too much magnesium compound remains in the light sensitive silver halide emulsion.

To produce gelatin while controlling the magnesium ion content, it is desirable to select an ion exchange resin, which is suitable for removal of the magnesium ions. For example, listed are, Amberlite IR-20, produced by Rohm and Haas Co., as a cationic ion exchange resin; Diaion SA-21A, produced by Mitsubishi Chemical Corp., or Dowex 1X8, produced by The Dow Chemical Co., as an anionic ion exchange resin;

and Diaion CR-20, produced by Mitsubishi Chemical Corp., as an amphoteric ion-exchange resin as well as a chelating resin. Various kinds of these ion exchange resins are available in the market.

As the foregoing substrates, almost any of the ones which are well-known in the art for photographic film may be employed. In this invention, specifically preferred is an acetyl cellulose ester substrate of acetylation degree of 2.6 - 3.0, which works to exhibit excellent improved effects.

For the foregoing photographic constitution layers, acceptable is an anti halation layer on the side closest to the substrate, as well as a red sensitive layer, a green sensitive layer and a blue sensitive layer, each of which comprises at least two layers, in addition to non-light sensitive layers. Preferably, each of the red sensitive layer and the green sensitive layer comprises three layers, each of different sensitivity. Further, the foregoing subbing layer preferably contacts the foregoing anti halation layer.

In the color photographic film of this invention, silver halide emulsions are employed. For example, employed may be the silver halide emulsions based on JP-A Nos. 61-6643, 61-14630, 61-112142, 62-157024, 62-18556, 63-92942, 63-

151618, 63-163451, 63-220238, and 63-311244, Research Disclosure (hereinafter, referred to as RD) 38057, Section I and III, and RD 40145, Section XV.

It is preferable to employ silver halide emulsions which are subjected to physical ripening, chemical ripening or spectral sensitization. Additives employed in these processing are described in RD 38957, Section IV and V, and RD 40145, Section XV.

Some of the photographic additives well known in the art, and employable in this invention, are described in RD 38957, Section II-X, and RD 40145, Section I-XIII.

To each of the red, green and blue sensitive silver halide emulsion layers of the color photographic film of this invention, couplers may be incorporated. The spectral absorption maximums of the developed dyes formed from couplers incorporated in each layer are preferably separated by at least 20 nm. As couplers, preferably employed are a cyan coupler, a magenta coupler and a yellow coupler. As combinations of each emulsion layer and the coupler, generally employed are combinations of a yellow coupler and a blue sensitive layer, a magenta coupler and a green sensitive layer, and a cyan coupler and a red sensitive layer, however,

they are not limited to these combinations, and other appropriate combinations may be employed.

In the present invention, a DIR compound may be employed. Specific examples of employable DIR compounds include D-1 through D-34 described in JP-A 4-114153, which are preferably employed in this invention. Further, other specific examples of employable compounds in this invention include, other than above, these described in U.S. Patent Nos. 4,234,678, 3,227,554, 3,647,291, 3,958,993, 4,419,886, and 3,933,500, JP-A Nos. 57-56837, and 51-13239, U.S. Patent Nos. 2,072,363 and 2,070,266, RD 40145, Section XIV.

Further specific examples of couplers employable in this invention are described in RD 40145, Section II.

Additives employed in this invention may be added using dispersion methods described in RD 40145, Section VIII.

In this invention, substrates well known in the art may be employed as described in the foregoing RD 40145, Section XV.

To the color photographic film of this invention, auxiliary layers such as a filter layer and intermediate layers may be provided, which are described in foregoing RD 38957, Section XI. The color photographic film of this invention may employ various layer structures of a

conventional layer order, an inverse layer order and a unit configuration, as described in foregoing RD 38957, Section XI.

The package of color photographic film of this invention may preferably be applied to common color negative film and color reversal film for color slides.

For color development of the color photographic film of this invention, developing agents well known in the art can be employed, as described in Theory of The Photographic Process Fourth Edition, pp. 291 - 334, and Journal of the American Chemical Society, vol. 73, No. 3, pg. 100 (1951), and the color film may be processed using common methods described in foregoing RD 38957, Sections XVII - XX, and RD 40145, Section XXIII.

EXAMPLES

The present invention will now be detailed with reference to examples, but the embodiments of the present invention are not limited to these examples.

Preparation of Sample 101

Onto one side of 120 μm thick acetyl cellulose ester film having an acetylation degree of 2.9, a methanol solution

of diacetyl cellulose (hereinafter, referred to as DAC) was applied, to provide a comparative subbing layer.

Subsequently, on the subbing layer, as photographic constitution layers described in the example (in paragraphs 0211 - 0222 of JP-A 10-20463), the 1st layer (being an anti halation layer) - the 15th layer (being a second protective layer) were applied to prepare Sample 101. The magnesium ion content of gelatin employed in each layer was 500 ppm.

Preparation of Samples 102 - 108

Samples 102 - 108 were prepared in the same manner as Sample 101, except that binder composition of the subbing layer was changed as shown in the following table. Furthermore, the ratio of gelatin/DAC in the table was brought to 60/40 (being a weight ratio).

Sample No.	Binder composition	Thickness (μm)	Mg ion (ppm)	Ca ion (ppm)
101	DAC	0.10	-	-
102	gelatin/DAC	0.040	1,200	1,500
103	gelatin/DAC	0.10	1,200	1,500
104	gelatin/DAC	0.40	1,200	1,500
105	gelatin/DAC	0.10	300	400
106	gelatin/DAC	0.10	600	100
107	gelatin/DAC	0.10	70	200
108	gelatin/DAC	0.10	25	200

Evaluation of Samples

The color photographic films of above Samples 101 - 108 were slit based on the standard of 135 mm size, 24 exp., and

then perforated, wound onto a spool, packed into a metallic film magazine, sealed into a moisture proof envelope formed of an aluminum-deposited film, Metaline Film ML-CPWH (produced by Tohcello Co., Ltd.), after which Samples were subjected to storage stability test, after which layer adhesiveness evaluation was conducted.

Evaluation 1: Evaluation of Storage Stability

Above Samples sealed at 23 °C and 50% RH were stored in a thermostatically controlled chamber with programmed temperature changes, and temperature changes of 1) - 6) in the following table was conducted at two cycles (for six days). Samples were placed on an aluminum plate so as not to contact each other. The duration to change to each temperature was 15 minutes.

1) at 8 °C for 12 hours
2) at 40 °C for 12 hours
3) at -20 °C for 12 hours
4) at 35 °C for 12 hours
5) at 8 °C for 12 hours
6) at 25 °C for 12 hours

Evaluation 2: Layer Adhesiveness Evaluation

Regarding each of Samples given the above storage stability test, the following layer adhesiveness evaluation was conducted.

(1) Layer Adhesiveness Evaluation of Dry Photographic Film

Each of Samples was stored under ambient conditions of 23 ± 2 °C and 50 ± 5% RH for 24 hours, after which 5 X 5 cells were formed of cut lines in a reticular pattern using a razor blade with 6 lines through the length and breadth at intervals of 3 - 5 mm, on the coated surface of the photographic constitution layers. A piece of 25 mm-wide cellophane tape was adhered onto the cells, after which the cellophane tape was rapidly peeled at the rate of 5 m/sec., and then, the ratio of the areas peeled by the adhered cellophane tape was evaluated based on the following criteria. A and B ranks are acceptable.

A: No peeling was observed.

B: Slight peeling at razor cuts was observed.

C: Less than 10% of the area was peeled off.

D: Between 10 - 50% of the area was peeled off.

E: More than 50% of the area was peeled off.

(2) Layer Adhesiveness Evaluation of Wet Photographic Film

Each of Samples of cut lines in a reticular pattern, as above (1), was soaked in a color developing solution (being a

color developing solution of Process C-41, produced by Eastman Kodak Co.) at 33 °C for three minutes, after which the surface having cut lines in a reticular pattern was uniformly scrubbed hard for 10 seconds by a hand while wearing a rubber glove. The ratio of peeled area in the hand scrubbed area was determined, and was evaluated based on the following criteria. A and B ranks were judged as acceptable.

A: Adhesion force was quite strong, and no peeling due to hand scrubbing was observed.

B: Adhesion force was very strong, and the peeled area was between 5 - 15% of the reticular pattern area.

C: Adhesion force was strong, and the peeled area was between 5 - 15% of the reticular pattern area.

D: The peeled area was more tan 15% and less than 50% of the reticular pattern area.

E: The peeled area was more than 50% of the reticular pattern area.

The obtained evaluation results are shown in the following table.

Sample No.	(1) Dry	(2) Wet	Remarks
101	C	D	Comp.
102	B	D	Comp.
103	B	B	Inv.
104	C	B	Comp.
105	A	B	Inv.
106	B	B	Inv.
107	A	A	Inv.
108	A	A	Inv.

Note: Comp.: Comparative example
Inv.: This invention

Industrial Applicability

As above, the present invention can provide a package of color photographic film which exhibits superior layer adhesiveness under dry as well as wet conditions, and also exhibits improved stability when stored under the various ambient conditions.